

SCIENCE FOR CERAMIC PRODUCTION

A paper by A. V. Belyakov and V. S. Bakunov titled "Stability of the Quality of Articles in the Ceramics Industry" was published in "Glass and Ceramics" No. 2, 1998, giving rise to a discussion on the problems of reproducibility of the quality of inorganic nonmetallic materials in the context of solution of the problem: "composition – structure – property."

The following paper continues the discussion of this problem. The data presented in this paper can be used in development of rational technological processes for production of ceramic articles with stable properties.

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THERMODYNAMIC ANALYSIS OF STRUCTURAL TRANSFORMATIONS IN SOLIDIFYING SYSTEMS

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Structural transformations in solidifying binder systems are considered in the context of the thermodynamics of irreversible processes. It is shown that the coagulation-condensation structure emerging in the binder system in the period of hydration acceleration is a dissipative structure. The emergence of instability in the binder system is accompanied by the development of oscillation phenomena, and the formation of a dissipative structure corresponds to an autowave process in the form of a standing electromagnetic wave. The structure formation schemes proposed in the paper make it possible to realize deliberate selection of external technological actions on binder systems.

The problem of obtaining materials with a reproducible structure and stable properties considered from the point of view of the thermodynamics of irreversible processes (synergetics) is important not only for ceramics production [1, 2], but for the production of mineral binders as well. Application of the thermodynamics of irreversible processes is especially promising for the study of structural transformations, since it has a greater degree of generality than kinetics, and does not use a hypothetical process model. It is precisely the thermodynamics of irreversible processes that makes it possible to analyze the general evolution laws in their physical aspect with a greater accuracy than could be done on the basis of classical thermodynamics [3].

The present paper demonstrates the opportunity of using nonequilibrium thermodynamics for the study of the structural transformations occurring in solidification of binders.

Solidification of binders, which is thermodynamically irreversible, is determined by the evolution of two interacting processes: hydrate formation and structure formation. The artificial stone emerging in this process evolves through a number of structural states which have different energy characteristics.

The fundamental principle of thermodynamic analysis of structural transformations in a binder system is the Prigogine – Glansdorff theorem on entropy production minimum P :

$$P = (1/T)(AJ_{\xi} + ZJ_h) \geq 0,$$

where T is the temperature; A is the chemical affinity; J_{ξ} is the rate of hydrate formation; Z is the structural affinity; J_h is the rate of structure formation.

The stability of a state of a system close to equilibrium is determined by the minimum value of entropy production. If a system is far from equilibrium, its stability is determined by the sign of excess entropy production $d_e P$: a state of the system is stable with a positive value of excess entropy production [3].

The structural states of a solidifying binder system not only have different thermodynamic stability, but also have different degrees of order, which predetermines the propensity of binder systems to ward self-organization. Self-organization is usually considered as the process of the origin and formation of increasingly complex spatial and time structures, i.e. an evolving process. Knowledge of the regularities of the evolution of binder systems makes it possible to delib-

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erately form the required spatial structures with specific operating properties in these systems.

Structure formation is the process of formation of interparticle contacts differing in type and strength in a solidifying system, where the nature of the contact varies during the process.

According to M. I. Shakhparonov, any thermodynamic processes can be expressed in terms of chemical reactions, therefore we represent the variations in the structural state of a binder system as a system of model quasireactions convenient for analysis:



where D are coagulation contacts; B are coagulation-condensation contacts; E are condensation-crystallization contacts.

Reaction (1) describes transformation of the coagulation contacts emerging in preparation of a binder dispersion into coagulation-condensation contacts, and reaction (2) describes autocatalytic formation of coagulation-condensation contacts due to degeneration of coagulation contacts. In combination with reaction (3) describing formation of condensation-crystallization contacts, these quasireactions are a bifurcation process of the chain reaction type. Since a coagulation-condensation structure is formed due to destruction of the preceding coagulation structure, reaction (2) reflects the development of destructive phenomena in the binder system. Calculation of the activation energy of the structure formation process in solidification of various binders showed that in the stage of formation of the intermediate coagulation-condensation structure, the activation energy decreases sharply, which is evidence of autocatalysis of the process.

In the context of the local nature of autocatalytic formation of coagulation-condensation contacts, diffusion inhibition is possible in the binder system, which in combination with autocatalysis results in bistability of the system. The latter is a prerequisite for the development of oscillatory processes in a binder dispersion. [4].

An appraisal of the stability of the structural states arising as a result of quasireactions (1) - (3) based on the value of the excess entropy production revealed [5] that the process described by reaction (2) makes a "dangerous contribution" to the excess entropy production, i.e. it results in perturbation of the stability of the state of the binder system.

In accordance with this reaction, a coagulation-condensation structure is formed. Consequently, this structural state is thermodynamically unstable and is a dissipative space-time structure, since its existence in time is limited.

The instability of the system and the origin of the dissipative structure are determined by the presence of a source of energy in a system or outside inflow of energy. In a

solidifying binder system, inflow of energy is provided by an endothermic hydration reaction, and maximum heat release is observed after the end of the induction period. Therefore, the formation of a dissipative structure is most probable in the period of acceleration of hydrate formation. The new hydrate formations arising in this period of solidification have different morphology, and morphological heterogeneity in a complex physicochemical system is the most significant factor of its nonequilibrium.

Morphological modifications of the new hydrate formations which take place in a solidifying system are accompanied by modification of their symmetry and energy release. This energy together with the hydration energy is instrumental in maintaining the nonequilibrium state of the binder system. The interdependence of formation of interparticle contacts and the morphological changes in a solidifying binder is an example of the coordinated processes that take place at different levels (macrolevel and microscopic level), which results in spontaneous self-organization. This self-organization is the totality of phase transformations of higher orders, since in this case no sharp modifications in the state of the system are observed. Since the structural transformations in a binder system take place within a certain range of thermodynamic parameter variation, they are diffuse phase transitions. However, it does not exclude the possibility of formation of a dissipative structure corresponding to a phase transition of the first order. In this case, the specified structure arises before "perishing" of the preceding structural state, i.e., each new structural organization step of the binder system is the embryo of its further evolution. An increase in the level of organization and complexity of the system promotes acceleration of its evolution [6], which agrees with model quasireaction (2).

It should be noted that the energy of internal processes (in our case, hydration energy or energy of morphological modifications of hydrates) can be low compared to the external action energy and yet sufficient for changing the process kinetics. Moreover, in exothermic processes, part of the heat energy released can be accumulated in structurally nonequilibrium fragments of the binding system, and at the same time be partially dissipated, which provides for energy accumulation required for the emergence of a dissipative structure.

According to [3], dissipative structures originate in nonequilibrium systems as a result of evolution of fluctuations. The usual fluctuations always present in a system cause a reaction that returns the system to the undisturbed state. However, in an instability area, fluctuations intensify due to energy "pumping up" and merge into a single long-lived fluctuation. This fluctuation encompassing the entire bulk of the system is the cause of a critical transition and the origin of a new structural state of the system. This structural fluctuation increases to macroscopic size comparable to the size of the binder system, and growth continues until the fluctuation is stabilized and acquires the form of a standing electromagnetic wave. Consequently, it can be inferred that

formation of a dissipative structure in a binder system is accompanied by the emergence of a standing electromagnetic wave in the system.

Perturbation of the stability of a binder system is accompanied by the development of oscillatory processes which play an important role in the evolution of binder systems. The oscillating processes can be generated by different mechanisms and, in particular, can constitute autowave processes. The latter is determined by the fact that hydrate formation and structure formation in certain stages of their evolution are autocatalytic processes, i.e. they not only determine, but also maintain the evolution of the binder system.

An essential contribution to the evolution of hydrate formation and structure formation processes is made by the active surface centers whose character and concentration determine the mechanism and rate of solidification of binder systems [7]. The contact embryos formed in the secondary active centers serve as the basis for the development of coagulation-condensation and condensation contacts. These contacts originate due to "elimination" of the contact embryos, and the following mathematical model consisting of a system of two differential equations is suggested for describing this process:

$$\begin{cases} \frac{dx}{d\tau} = -ax + bxy, \\ \frac{dy}{d\tau} = cy - dxy, \end{cases} \quad (4)$$

where x is the number of coagulation-condensation contacts; y is the number of contact embryos; a, b, c, d are positive constants.

The summand (bxy) expresses an increase in the number of contacts depending on the number of embryos, and the summand ($-ax$) reflects the decrease in the number of embryos as contacts are formed from them. Since part of the emerging contacts can be destroyed, the summand ($-ax$) expresses the number of "perishing" contacts. The summand (cy) expresses the "birth" of contact embryos in active centers of solid particles. Thus, coefficients a and b are the constants of "mortality" and "birth rate" of contacts, and c and d are the similar constants for contact embryos.

Numerical modeling of system (4) showed that the numbers of contacts and embryos experience variations, and the phase curve corresponding to model (4) is an unstable focus which is transformed into a limiting cycle. It corresponds to the development of autowave processes in the binder system. These processes only occur in active environments characterized by disperse energy inflow, on account of which they exist in a state far from thermodynamic equilibrium. Thus, the results of analysis of system (4) also point to the onset of instability in a binder system on appearance of coagulation-condensation contacts in it. These autowave processes in binder systems can be of two types: ring waves and spiral waves.

The sources of ring waves are active centers corresponding in their properties to high-velocity surface electron states [8]. Therefore, an active center is an energy generator with a natural oscillation frequency, known as a pacemaker. If a system contains pacemakers with different frequencies, they compete, and as a result, the pacemakers remaining in the system are those generating ring waves with the maximum frequency. Therefore, the active centers in a binder system are "selected" in the stage of existence of a dissipative structure. As in this stage of solidification, the active centers are mostly concentrated on the surface of the new hydrate formations, and the selection specified is related to a change in hydrate morphology. Finally, the morphological forms of hydrates that are selected are best suited to the functioning of the binder system.

The sources of spiral waves are condensation contacts formed in the binder system as a result of structural fluctuations. All spiral waves in the given system have the same frequency, therefore they do not suppress each other and are attracted while spinning in opposite directions. A spiral wave is a variety of traveling wave, and on their interaction, a standing wave is formed. The latter is stable only with "pumping up" of energy, which is also typical of the existence of a dissipative structure. Consequently, formation of a dissipative structure in a binder system is related to an autowave process in the form of a standing wave arising as a result of the interaction of spiral waves.

The analysis of the changes in the structural states of various binder system (gypsum binders, mono- and polymineral cements, mixed cements) and their thermodynamic stability performed on the basis of the regularities described above indicated that its results do not disagree with the known concepts of structure formation in solidifying systems. The results of this analysis in combination with the available data on the kinetics of hydrate and structure formation established that the structure formation process in binder systems can evolve according to one of three schemes.

The first scheme is characterized by monotonic structure formation, when the degree of process completion is an increasing function over the entire time interval of hydrate formation. This scheme corresponds to structure formation in gypsum binders and the most reactive mineral binders (CaO , $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, etc.) with a short induction period. A typical feature of these binder systems is kinetic synchronism of the hydrate and structure formation processes, which determines the formation of a thermodynamically stable coagulation or pseudocondensation structure with point contacts in these systems. Hydrate formation in these binders does not have an autocatalytic stage, therefore the state stability of the system is not disturbed even in the case of its substantial deviation from equilibrium due to the exothermic reaction of hydration. Moreover, these binder systems are characterized by the morphological homogeneity of new hydrate formations, which is another factor determining the stability of their structural states.

The second scheme, that of a single-stage structural formation, is typical of silicate minerals: Portland cement, Portland and slag-Portland-cement. In this pattern, the increase in the degree of completion of structure formation related to the formation of a coagulation structure is followed by its decrease, which is determined by destruction of the coagulation structure due to acceleration of the hydration process. The processes of hydrate formation and structure formation in this period of solidification are autocatalytic, which results in the appearance of a dissipative space-time structure. This structure is a variety of autowave processes, and its emergence is attended by the appearance in the binder system of a standing electromagnetic wave recorded experimentally. The origin of the thermodynamically unstable structural state in solidification of these binders is also determined by the morphological heterogeneity of their new hydrate formations. Slowing of the hydration process results in disappearance of the dissipative structure, and a condensation-crystallization structure that is thermodynamically stable is formed in the binding system, which is accompanied by a monotonic increase in the degree of completion of structure formation.

The third scheme is multistage structure formation. It is typical of mixed cements whose variation curve of the degree of completion of structure formation has several extremes.

The multistage structure formation arises as a complex superposition of chemical reactions separated in time and interacting with the single process of structure formation. In this case, structural states of the same type periodically emerge in the binder system, and the number of structure formation steps depends on the ratio of the hydraulic activity components and their amount in the mixed cement. Due to the variety of chemical reactions that takes place in solidification of mixed cement, several instability areas and, consequently, various dissipative structures arise in the binder system. The dissipative structures differ in their scale and period of existence, which is determined by the energy of the hydrate formation and structure formation processes. The instability of the structural states in the binder systems with multistage structure formation is determined by the significant morphological heterogeneity of the new hydrate formations.

Owing to the dual character of the reactivity of the binders, in modification of the solidification conditions the scheme of structure formation is modified as well, which is accompanied by modification of the thermodynamic stability of the structural states. The latter is regularly related to changes in the phase composition and structure of the new

hydrate formations. From these facts follows the need of observing the self-organization principle, according to which it is possible to conduct a spontaneous process in a prescribed direction only in the case of coordination between the external action and the internal processes.

The implementation of this principle is possible on the basis of the proposed structure formation schemes which permit determination of the stages of the solidification process, where technological actions should be performed. The rational parameters of the action procedure are assigned based on a thermodynamic evaluation of the result of their effect on the structure formation process.

The structure formation of ceramics is also accompanied by a change in the character and strength of the interparticle contacts, therefore, in the course of this process, the unstable structural states constituting the dissipating structure can emerge. These structural states are most susceptible to external actions, and protracted sustaining of a nonequilibrium state in a ceramic system can cause not only local disturbances, but also in a complete destruction of the structure. Thus, the above analysis of the thermodynamic stability of the structural states of solidifying systems makes it possible to determine the stages of structure formation suitable for external actions and can be used for the development of rational technological processes to produce ceramics with stable properties.

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